

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
30 August 2001 (30.08.2001)

PCT

(10) International Publication Number
WO 01/62843 A2

- (51) International Patent Classification⁷: C08L
- (21) International Application Number: PCT/US01/05727
- (22) International Filing Date: 22 February 2001 (22.02.2001)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
09/511,668 23 February 2000 (23.02.2000) US
- (71) Applicant (*for all designated States except US*): LU-MIN-OZ, LLC [US/US]; 8460 Higuera Street, Los Angeles, CA 90232 (US).
- (72) Inventors; and
- (75) Inventors/Applicants (*for US only*): PERRY, Michael, S. [US/US]; 8145 Laurelmont Drive, Los Angeles, CA 90046 (US). LANTZ, Daniel, W. [US/US]; 8145 Laurelmont Drive, Los Angeles, CA 90046 (US).
- (74) Agent: MEIER, Paul, H.; Lyon & Lyon LLP, 633 West Fifth Street, Suite 4700, Los Angeles, CA 90071-2043 (US).
- (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
- Published:
— without international search report and to be republished upon receipt of that report
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*



WO 01/62843 A2

(54) Title: EXTRUDED SHEET WITH CONTROLLED SURFACE GLOSS AND PROCESS FOR THE MANUFACTURE THEREOF

(57) Abstract: Extruded thermoplastic or thermoset sheet capable of transmitting light with upper and lower, or rear and front, surfaces exhibiting markedly different degrees of gloss such that one surface is high gloss, shiny and smooth, while the other surface is low gloss and matte; and related products and articles, and processes for producing such materials.

DESCRIPTION

Extruded Sheet With Controlled Surface Gloss And Process For The Manufacture Thereof

Background Of The Invention

5 Matte-surface or low-gloss polymers are thermoplastic or thermoset materials that scatter light broadly from the surface rather than having a glossy surface with high reflectance. They may be clear, opaque, tinted or colored, and may be formed into films or sheets of various thicknesses or into more complicated shapes or articles.

10 Commercial production of thermoplastics with surface alteration to reduce gloss has been performed for many years. This has been done by such manufacturing techniques as the use of specially roughened or embossed casting or calendering rolls, extrusion under conditions producing melt fracture such as is taught for acrylic film in U.S. Pat. No. 3,415,796, and the use of small particle size inorganic fillers (flatting agents), such as silica and calcium and magnesium silicates, and thermoplastic particles.

15 The first technique requires special processing equipment, does not allow easy variation of the degree of gloss reduction achieved, and often lacks uniform quality; the second requires materials of low melt flow which places an additional load on the extruder, and it is difficult to avoid a patterned or "sharkskin" appearance from excessive melt fracture; the third can often cause wear on thermoplastic processing machinery and/or cause

20 deterioration of the physical properties of the resultant plastic such as loss of impact strength, toughness, clarity, processability and so on, and the particles are often difficult to disperse.

 Polymeric modifiers for alteration of surface properties known in the art include the use of acrylonitrile-butadiene-styrene (ABS) resins produced such that one resin

25 component comprises ABS polymer particles crosslinked to such a degree that they maintain their shape even during the extrusion process, thus producing surface-alteration. Similar technology for polyvinyl chloride uses crosslinked PVC beads similar in size to the uncrosslinked resin (Japanese Kokai 83-33426), giving surface protrusions 1-45 μm in height. Another useful technology (Lang, U.S. Pat. Nos. 3,992,486 and 4,000,216)

30 comprises bulk or suspension polymerization of a monomer mixture containing a crosslinking monomer in the presence of a dissolved preformed polymer under conditions wherein the new polymer is formed as particles of broad size distribution in the range of 1 to 30 μm dispersed in a continuous phase of the preformed polymer. These particles

dispersed in the preformed polymer are then processed with a suitable polymeric matrix to achieve a desired flatted, matte-surfaced, or low-gloss plastic.

Each of the above methods has been reported to suffer from at least one of the following problems: lack of ability to adjust the refractive index and hence the optical properties of the resultant blend, hard particles resulting in poorer impact strength, poor dispersion of the particles in the matrix polymer with accompanying degradation of the physical properties of the matrix polymer, and reduction of light transmission in the matrix polymer. In contrast, U.S. Pat. Nos. 5,237,004 and 5,346,954 (Wu et al.), which are incorporated herein by reference, describe the use of particles that have a rubbery core, and optionally a thermoplastic shell, that disperse well in the polymer matrix without causing undue deterioration of the impact strength or physical properties of the matrix polymer, and that also allow the refractive index of the core polymer to be adjusted such that the refractive index can be varied over a wide range to allow materials to be produced without excessive degradation of the light transmission in the matrix polymer and also to produce matte or flatted surfaces with low gloss.

While the production of low-gloss surface sheet and articles is well known in the art, the surfaces of the fabricated sheet or article generally have gloss values in the same range. Thus, for example, a sheet which has high gloss on the upper surface also has substantially similar high gloss on the lower surface unless the degree of gloss is subsequently altered by a mechanical process such as abrasion, buffing or sand blasting, or by heat or solvent treatment or other auxiliary methods. For example, in U.S. Pat. No. 5,264,164 (Pickett et al.), an auxiliary die is used after the extrusion die and the degree of gloss of the decorative surface is then altered and controlled by varying the temperature of the auxiliary die relative to the extrusion die. In this process, the temperature of the auxiliary die, which is of a thermally unitary metal structure, is made higher than that of the extrusion die to increase the degree of gloss of the decorative surface, and it is made lower than that of the extrusion die to reduce the degree of gloss. However, the use of this process taught in the '164 patent is as a method for altering the gloss of the extrudate from that obtaining when the sheet comes out of the primary extrusion die, rather than as a method for generating differential gloss on each side of the extruded sheet or strip. The patent does not suggest that different portions of the auxiliary die should be maintained at different temperatures, and does not provide any means to do so. Accordingly, the patent does not teach any method or apparatus for generating differential gloss on each side of the extruded sheet or strip. In addition, this method is cumbersome in that it requires non-standard manufacturing equipment; the auxiliary die must be of such size and shape as to receive the extrudate from the extrusion die without further deformation of the

profile, such that the process is limited in the width of material that it is practicable to process and is largely applicable only to narrow strips.

It is an object of the present invention to provide articles such as sheet and products derived from such sheet which have differential gloss surfaces, e.g. markedly
5 different gloss levels on the upper and lower surfaces of such sheet, directly from the extrusion and sheet casting process without the necessity of using secondary processing methods after the production of the said sheet. The invention also allows wide widths of sheet to be processed with standard sheet casting equipment, and provides a process for the production of such sheet and products derived from such sheet. It is a further object of
10 the invention to provide such sheet and derived products with differential gloss surfaces substantially without causing deterioration of the physical properties of the product.

Another object of the invention is to provide articles, and products such as composite sheet viewing screens and optical projection systems such as rear-projection television sets and front-projection viewing systems, incorporating the screens and other
15 materials of the invention.

The invention further provides processes for manufacturing the screens, materials and related articles and products of the invention.

It is yet another object of the invention to provide sheets, viewing screens and similar materials having improved optical characteristics, particularly optical image
20 viewing characteristics useful in a variety of commercial and consumer contexts.

Summary Of The Invention

The invention is described below and certain aspects of the invention are presented in the claims. Some of the more significant aspects include novel sheet and other articles exhibiting a marked differential in surface gloss characteristics between different surfaces
25 of the product, particularly in products that are light-transmissive (capable of passing or transmitting light therethrough).

The invention involves thermoplastic or thermoset polymer sheets and other articles, and particularly thermoplastic sheets, containing optically active and preferably optically refractive particles (especially polymer particles) that provide light diffusive
30 properties and superior optical viewing properties compared to materials that do not exhibit the surface gloss differentials taught herein.

The invention provides materials that are readily manufactured according to the processes described, and that can readily be transformed into products that are useful to consumers and industry. Examples of such products include consumer and commercial
35 viewing screens with improved image presentation characteristics. The images can be

projected from a light projecting apparatus, or can be applied via other optical presentation means well known in the art.

Processes for obtaining the products of the invention are described. In one aspect, the manufacturing process includes means for receiving hot extruded thermoplastic or other material and applying a differential heat transfer to different surfaces thereof, to achieve surfaces having different high-gloss and low-gloss, and preferable optically transmissive, characteristics.

Numerous other aspects of the invention will be seen in the following disclosure.

Detailed Description

10 The present invention relates, in one aspect, to an extruded thermoplastic or thermoset sheet capable of transmitting light, having upper and lower (or, equivalently, front and rear) opposing surfaces exhibiting markedly different degrees of gloss. The invention further relates to shaped articles and other products derived from such sheet products, and processes for producing such materials.

15 In one aspect of the present invention, a thermoplastic or thermoset polymer composition sheet or article is provided having a reduced-gloss or matte surface finish on one surface only so that there is a significant differential between the gloss values of the two surfaces of the sheet or article. Preferably, the differential in gloss values, when measured at an angle of 85° using a glossmeter by the method of ASTM D532, is at least about 40, more preferably at least about 50, and still more preferably at least about 60. In one preferred embodiment of the invention, the high-gloss surface has a gloss value (measured at 85°) greater than about 70, and the low-gloss or matte surface has a gloss value less than about 30. The low-gloss characteristics of the matte surface are not due to mechanical shaping (such as Fresnel or other lenticular shaping) nor to the addition of a separate low-gloss coating material to that surface, but rather arise from the properties of the processed polymer composition itself. Nevertheless, it will be recognized that surface or surfaces of the sheet may be separately shaped or modified after the sheet is initially manufactured. Such sheets and products made from them are particularly useful as screens for viewing optical images, whether still or moving. The sheet is preferably composed of materials that allow transmission of light applied to one surface, as for example light from a projected optical image, through the body of the screen and out through the opposing surface.

Such sheets and related articles provided in accordance with this aspect of the present invention comprise thermoplastic or thermoset polymer compositions capable of transmitting (i.e. passing) light therethrough, and having a reduced-gloss or matte surface

finish on one surface. These thermoplastic or thermoset polymer compositions preferably comprise a thermoplastic or thermoset matrix polymer and, distributed throughout the matrix polymer, particles constituting from about 0.1 to about 50%, preferably from about 1 to about 40%, and in many optical contexts preferably about 10 to about 40% of the total composition weight. The particles are selected so as to be capable of diffusing light as it passes through the sheet, and preferable are optically refractive particles. Especially preferred are polymer particles, and preferably substantially spherical polymer particles, having an average diameter of from 1 to 30 μm , preferably 2 to 15 μm , and more preferably 5 to 10 μm , wherein the particle size distribution is preferably such that at least 90% of the particles fall with $\pm 20\%$ of the average particle diameter.

The matrix polymers useful in the present invention are preferably, but not limited to, thermoplastic polymers that do not crystallize under processing or use conditions and that have a glass-transition temperature higher than about 50°C, and thus are amorphous following incorporation of the above polymeric particles and remain amorphous following processing to form the differential surface gloss articles of the present invention. These matrix polymers and the extruded sheet produced from them by the process of the present invention have modulus values such that they may be used as is or optionally formed into shaped articles by molding, thermoforming, vacuum forming or other processes apparent to those skilled in the art without substantially altering the differential gloss of the surfaces. The sheet of the invention may also be laminated or otherwise attached at one or both surfaces to another sheet or surface to form a composite sheet or article.

Examples of such matrix polymers include homopolymers and copolymers of methyl methacrylate, styrene, vinyl chloride, vinyl acetate and the like, imidized polymers of methyl methacrylate, and copolymers of methyl methacrylate with alkyl acrylates, styrene with up to 40% acrylonitrile, styrene with methyl methacrylate, acrylonitrile or maleic anhydride, alpha-methylstyrene with methyl methacrylate and/or alkyl acrylates, vinyl chloride with vinyl acetate or propylene, acrylonitrile-butadiene-styrene, methyl methacrylate-butadiene-styrene, and the like, or impact-modified versions of the above. Also suitable are cellulose acetate butyrate and other cellulose esters, condensation polymers such as poly(ethylene terephthalate), poly(cyclohexanedimethanol terephthalate) and other polyalkylene terephthalates and the like, cyclo-olefin copolymers, polysulfone polymers, polyolefins, such as polyethylene, polypropylene or polymethylpentene, and engineering resins, such as polycarbonates, polycarbonate-polyester blends, polyamides, polyurethanes, phenol-type resins, and blends or impact-modified versions thereof. Preferred matrix polymers are copolymers of methyl methacrylate with from about 1 to about 15% alkyl acrylates, wherein the alkyl group contains from 1 to 8 carbon atoms.

The spherical polymer particles are incorporated into the matrix polymers preferably by melt blending, although other techniques known to those skilled in the art may be employed. For instance, they may be introduced dry into the monomers of the matrix polymer prior to their polymerization. Other additives, such as ultraviolet-light
5 stabilizers, flame retardants, thermal stabilizers, plasticizers, processing aids, impact modifiers, pigments, dyes, fillers and the like may also be present in the blend of spherical polymer particles and matrix polymer.

Mixtures of the particulate and matrix polymers and optionally other additives may be blended and extruded into pellets, which then are extruded and processed directly into
10 sheet or film. Alternatively, the pellet production step may be omitted and the particulate and matrix polymers and optionally other additives may be compounded in-line and extruded and formed into sheet as a single continuous operation.

Another class of matrix polymers useful in the present invention are thermoset polymers. These polymers may be thermoset as prepared, such as in casting of a sheet of
15 poly(methyl methacrylate) containing sufficient polyfunctional monomer to immobilize and insolubilize the resulting sheet, or the polymer may be thermoset after polymerization is completed, such as by activating a cure reaction by heating of the polymerized sheet. Examples of such thermosettable matrix polymers include homopolymers of methyl methacrylate, styrene, vinyl chloride and the like, imidized polymers of methyl
20 methacrylate, and copolymers of methyl methacrylate with alkyl acrylates, styrene with up to 40% acrylonitrile, styrene with methyl methacrylate, alphas-methylstyrene with methyl methacrylate and alkyl acrylates, vinyl chloride with vinyl acetate or propylene and the like. Preferred matrix polymers are copolymers of methyl methacrylate with from about 1 to about 15% alkyl acrylates wherein the alkyl contains from 1 to 8 carbon atoms and
25 which also contain di- or poly-functional acrylate or methacrylate monomers at the 0.05 to 2% level, or which contain acrylamide and N-methylolacrylamide at the 0.05 to about 5% level. Other secondary crosslinking mechanisms may also be incorporated into the formulation.

The thermoset polymers need not be formed from vinyl monomers, but may be
30 prepared by condensation or ring-opening polymerization, such as by polyesterification in the presence of multifunctional glycols or by epoxide polymerization in the presence of trifunctional epoxides.

The particles useful in the invention are preferably substantially spherical and comprise individual particles with a diameter from about 1 to about 30 μm , preferably 2 to
35 about 15 μm and more preferably from about 5 to about 10 μm , and preferably having a narrow particle-size distribution. The preferred particle size distribution is preferably such

that at least 90% by weight of the particles fall within $\pm 20\%$ of the average diameter of the particles; it is understood that the term "particle size distribution" used herein refers to the size range of at least 90% by weight of the particles. Particle size may be determined by any conventional means, as for example by using a Coulter Counter, Nanosizer or optical
5 or electrical microscopy. The particles serve to diffuse light as it passes through the sheet of the invention, and also contribute to the low-gloss characteristics of the matte surface of the sheet. The particles are preferably optically refractive, with an index of refraction selected as described herein.

Polymer particles are especially preferred in the practice of the invention. Such
10 polymer particles may, for example, be prepared from one or more vinylic, acrylic or methacrylic monomers, and may be a rubbery or glassy polymer, or both. The spherical polymer particles may be prepared from polymerization or copolymerization of such monomers as diolefins, such as butadiene or isoprene, vinyl aromatic monomers, such as styrene or chlorostyrene, vinyl esters, such as vinyl acetate or vinyl benzoate, acrylonitrile,
15 methacrylonitrile, (meth)acrylate esters, such as methyl methacrylate, butyl methacrylate, phenyl methacrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, benzyl acrylate, vinyl chloride, and other common monomers polymerizable by free-radical initiation. The copolymers also include polymers made by staged addition of monomers, so that the spherical polymer particles may not necessarily be uniform in composition. Suitable
20 core-shell polymer particles are also commercially available, as for example "Paraloid" core-shell impact/surface modifier products available from Rohm and Haas Corporation, and similar core-shell products from other manufacturers. Such core-shell particles may comprise more than one shell and more than one polymeric phase in the core of the particles. Preferably, at least the outer shell of such core-shell particles is compatible with
25 the matrix polymer in which the particles are contained, such that the outer shell is miscible or compatible with the matrix polymer so as not to produce structural gaps, or reflective or other barriers to the transmission and diffusion of light.

Differential gloss surfaces can also be obtained according to the present invention using opaque or filled thermoplastic or thermoset matrix polymers by incorporating in
30 them the spherical polymer particles. However, for many of the applications of the invention, including front- and rear-projection viewing screens and other optical products, it is preferred that the screens and other products of the invention be able to pass light therethrough, and that the polymer matrix and particles be chosen accordingly as described herein.

35 For example, by carefully matching the refractive index of the particles to the refractive index of a light-transmissive thermoplastic or thermoset matrix polymer, either

light-scattering polymer compositions capable of diffusing light, or substantially clear polymer compositions, can be obtained, in both cases having differential gloss values on each surface. Moreover, such compositions can be obtained which show no substantial deterioration in impact resistance, melt flow or other physical or rheological properties of the matrix polymer versus an unmodified control. Preferably, if the final thermoplastic or thermoset polymer composition is to be light-scattering, then the spherical polymer particles will comprise at least one polymeric phase which has a refractive index (n_D^{25}) within about ± 0.2 units of, but preferably no closer than about ± 0.003 units to, the refractive index of the matrix polymer. If the thermoplastic or thermoset polymer composition is to be substantially clear or transparent (other than at the matte surface), then the spherical polymer particles will preferably comprise at least one polymeric phase which has a refractive index within about ± 0.003 units of the refractive index of the matrix polymer. If the spherical polymer particles comprise a polymeric core phase and one or more polymeric shell phase(s), i.e. a core-shell polymer, rather than a single polymeric phase, and if the thermoplastic or thermoset polymer composition is to be substantially light-scattering or clear, then at least the polymeric core phase of the core-shell polymer preferably has the respective refractive index values described above.

The amount of particulate polymer to be incorporated in the matrix polymer will depend upon the surface and optical effects desired, the thickness of the final fabricated article and its desired physical properties, the particle size distribution and the difference in refractive index between the particle and the matrix polymer. A practical useful range for the spherical polymer particles is preferably from about 0.1 to about 50% of the total polymer weight, preferably from about 1 to about 40%, and in many optical contexts preferably from about 10 to about 40% by weight of the total composition.

It is believed that increased particle levels generally allow a higher reduction in gloss on the matte surface while also (depending on the indices of refraction) increasing the diffusion or scattering of light as it passes through the screen. In the context of an optical viewing screen that is exposed and susceptible to scratches and the like, it is desirable that the low-gloss, matte sheet surface be the exposed surface because it will hide the visual effects of scratching more so than a high-gloss surface. For optimum image presentation and to maintain modulus of the sheet, however, the particle amount may be adjusted significantly below the upper limit of about 50% by weight. Thus, the level of incorporated particles in a sheet for use in a typical optical screen context is preferably in the range of about 10% to about 40% of the final composition, since below a level of about 10%, color saturation begins to be lost, while about a level of about 40% the modulus and the ability to be viewed in situations with high ambient light levels also

decrease. By way of example, a 1 mm thick sheet of the invention incorporating about 20% by weight polymer particles has been found to work extremely well in a rear projection viewing screen context, in which the image is projected onto the high-gloss side of the sheet and the normal viewing side is the exposed matte side of the sheet. Such a material also works extremely well in a front projection system in which the image is projected onto and viewed from the matte side of the sheet. Optimum amounts of particles and other components can readily be determined for a particular product configuration using the teachings of the present disclosure.

The surface-altered or matte-finished or low-gloss compositions and articles comprising the light-diffusive compositions of the present invention are especially useful for surfaces of molded or shaped objects where low reflectance is desired, especially where an optical image of fixed or changing content is projected or otherwise applied by light to the article for viewing purposes, and particularly in high ambient light and direct light environments. Examples of such use are video projection screens which hide imperfections, damage, abrasions and scratching during viewing, including screens in consumer products as well as large commercial screens as may be employed in an advertising, stadium or similar environment; rear projection screens such as those used in rear projection television sets and similar rear projection viewing systems; anti-glare front projection screens for brightly lit environments; computer screens and other displays wherein light-emitting or light-passage-controlling devices (such as light emitting diodes or liquid crystal devices) are adjacent to or affixed directly to the screen, as for example in a pixel matrix; signage; shaped articles produced by thermoforming and similar methods wherein the matte surface texture is retained after forming without change in the gloss values or texture separation, even in areas where drawing occurs; and aesthetic designs such as lampshades, sconces, and table and bar tops where the matte finish effectively diffuses the light source behind, within or in front of the decorative feature. Examples of such applications are noted in U.S. Pat. Nos. 5,170,287 and 5,307,205 (both to Ludwig, Jr. et al.), albeit with no teaching of the valuable feature of differential gloss on the front and rear sheet surfaces which is one of the objects of the present invention.

The extruded sheet of the present invention may be used as a single layer sheet or may also be laminated or otherwise attached on either or both the glossy or matte surfaces to additional sheets of the invention or to surfaces of other materials to provide composite sheet or articles. Such attachment may be achieved by adhesion, bonding, heat pressing, welding or other methods apparent to those skilled in the art. For example, a sheet of the invention may be attached to a second sheet that provides additional rigidity, and thus strength and support, in the composite sheet structure. Where the second sheet is also

optically transmissive, as for example a clear acrylic sheet laminated to the "rear" high-gloss surface of the sheet of the present invention, the composite sheet may be used as a rear projection viewing screen, while also functioning well with front-projected images projected onto the "front" matte side of the sheet.

5 The improved optical and other characteristics of the present sheets and related articles and products is attributable to the presence of both a matte surface and, opposed to it, a high-gloss, smooth surface. As explained above, the matte surface hides scratches and the like and displays projected images well. The high-gloss surface provides a superior surface for transmitting images therethrough without distortion, and also for
10 laminating or otherwise attaching the sheet to another substrate, as for example a smooth, clear acrylic sheet. As opposed to dual-matte-surface materials, the high-gloss surface of the present sheet can readily be attached to such a substrate using, for example, a very thin film of adhesive that is effectively optically transparent. Due to the smoothness of the high-gloss surface, such a thin layer of adhesive will distribute evenly between the mating
15 surfaces without bubbles, "fish-eyes" or other visible or optical irregularities, while still providing enough adhesive to effect a strong bond to the substrate.

 The surface-altered, differential gloss materials of the invention may also be used in films or sheets requiring one low-gloss surface to improve printability or hiding of surface imperfections or requiring a slightly roughened surface for improved adhesion, or
20 they may be used to reduce adhesion between surfaces and so to prevent blocking. Pigments, dyes, fillers, impact modifiers, stabilizers, ultraviolet light stabilizers, thermal stabilizers, plasticizers, processing aids, flame retardants, and other additives etc. may be added to the formulation to achieve appropriate manufactured articles. For example, tints such as gray tint may be incorporated into the sheets of the invention to improve image
25 contrast where the article is to be used as a viewing screen, and ultraviolet stabilizers may be added to prevent the sheets yellowing over time.

 For uses where clarity or transparency is desired, narrow-size-distribution particulate polymers within a relatively narrow particle size range of about 2 to about 10 μm where the refractive index is carefully matched with the substrate exhibit excellent
30 flattening performance on the matte or low-gloss side while maintaining good contact clarity from the smooth higher-gloss surface on the other side. For uses where clarity is not essential, it is not necessary to supply the refractive index match within the close tolerances taught herein, although such may be desired for best pigmentation effects.

 It will be understood by those skilled the art that the sheets of the present invention
35 are typically thin, flat articles produced by extrusion processes that lead directly to the differential surface gloss characteristics of the resulting sheets, without need for further

processing (e.g. lenticular shaping) or surface treatment (e.g. layering of a separate material onto either surface). However, the dimensions of the articles of the invention may vary, and articles having substantial thickness such as bars, plates and the like, as well as three-dimensional articles such as molded articles, may be produced using the methods described herein. Furthermore, one or more surfaces of the described sheets and related articles may be modified, as by coating or lenticular shaping, to further adjust their optical and gloss characteristics.

The differential gloss extruded sheets and related articles of the invention are typically produced by exposing different (e.g. upper and lower) surfaces of the hot extrudate sheet or article, composed of a polymer composition as described herein, to one or more receiving surfaces that cause differential heat transfer with the respective sheet surfaces. For example, a thermoplastic composition as described herein can be extruded through a melt extruder system and die to form a hot extrudate sheet which is then cast (preferably while still hot, or reheated as necessary) onto a casting roller or system of rollers, wherein the temperatures of the extrusion die, the extrudate sheet and the casting roller(s), and the contact time with the casting roller(s), are adjusted to achieve differential heat transfer with the upper and lower surfaces of the extrudate sheet. At least one of the receiving surfaces is preferably maintained at a temperature lower than, and preferably at least 20°C lower than, the glass transition temperature of the thermoplastic composition so as to provide a product sheet that has one surface that has a low gloss value and appears matte, and another surface that has a relatively high gloss value and appears shiny and smooth. The polymer composition and resulting product preferably is amorphous and contains polymer particles within a thermoplastic matrix polymer, for example a methyl methacrylate polymer optionally further comprising a copolymerized alkyl acrylate, as described herein.

In one representative extrusion/casting configuration, a hot thermoplastic extrudate sheet (for example a methyl methacrylate-containing polymer composition) is extruded from a heated extrusion die (heated for example to about 200-270°C, or more preferably 210-250°C, depending upon the glass transition temperature and melt characteristics of the matrix polymer) and then directly passed between the lower roller and the middle polishing roller of a three-roller casting system, having a nip between the two rollers adjusted to the desired sheet thickness. At least one of the lower and middle rollers, and preferably at least the middle polishing roller, is maintained, for example by water cooling, at a temperature below the glass transition temperature of the thermoplastic composition, for example a temperature at least 20°C or preferably at least 30°C below the glass transition temperature (e.g. in the range of 5-70°C). Alternatively, one of the two

initial rollers (preferably the lower roller) may be heated while the other roller is maintained at the lower temperature. The sheet is then rolled around the middle polishing roller, with a first sheet surface in thermal contact with the polishing roller and the second opposing surface not in contact, so as to provide differential heat transfer with the opposing surfaces of the extrudate sheet. The sheet typically traverses approximately 180° of rotation about the polishing roller, and then is passed onto the third (here, upper) roller of the stack where the second sheet surface contacts the third roller through a rotation angle of, for example, 270° rotation. The third roller may likewise be maintained at a temperature below the glass transition temperature, or alternatively it may be heated to modify the gloss characteristics of the resulting sheet. Given the teachings of the present disclosure, those skilled in the art will readily be able to identify extrudate and roller temperatures, contact times and processing speeds that will result in sheets and similar articles as described herein.

In the case of a thermosetting polymer composition, processing conditions can similarly be identified by those skilled the art given the present teachings. For example, a hot thermosetting polymer composition, and preferably one containing polymer particles as described herein, may be cast as a sheet onto an appropriate receiving surface having a temperature adjusted so as to provide differential heat transfer with the contacting and non-contacting sheet surfaces, and then thermoset so as to provide a product sheet having the differential gloss characteristics described herein.

Examples

The following examples are meant to illustrate aspects of the invention, and some of the ways of accomplishing it. Alternative ways of accomplishing the invention of this patent will be recognized by those skilled in the art, given the disclosures herein. The examples do not limit the invention, which is set forth in the claims below and extends to all lawful equivalents of the subject matter claimed.

Example 1

A mixture containing 80% commercial acrylic molding resin DR-101 (Rohm and Haas), which is a methyl methacrylate polymer containing a small amount of copolymerized alkyl acrylate and having a melt flow rate of about 1 g/10 min measured under Condition 1 of ASTM D-1238 and about 20% of a core shell impact/surface modifier (Paraloid EXL 5136; Rohm and Haas) was dry blended and then compounded in a twin screw extruder to produce pellets using a strand die at a melt temperature of about 240°C. These pellets were then dried and extruded at a melt temperature of about 230°C

through an approximately 66-inch wide flat sheet die. This still-hot extrudate sheet was then directly passed between the first roller and the middle polishing roller of a vertical 3-roll coated roll stack set with a nip setting of 1 mm. The sheet was rolled around the polishing roller and then passed around the final roller to produce the product sheet. The temperatures of the three rollers in the stack were kept at or below about 50°C to produce a flat sheet with a high-gloss surface and an opposing matte surface. The differential in temperatures between the sheet and the rollers, which causes a differential heat transfer between the sheet surface exposed to the roller and the sheet surface opposing it, led to the product sheet having different surface gloss values as described herein. Gloss values were measured on both sides of the product sheet according to ASTM D532 using a Gardner Micro-Tri-Gloss glossmeter at 85° and also 60° angles to give the gloss values shown below:

85° Gloss Measurement Angle:

Matte Side: 23.9 (mean) (standard deviation = 2.1)

Gloss Side: 84.7 (mean) (standard deviation = 2.7)

60° Gloss Measurement Angle:

Matte Side: 13.4 (mean) (standard deviation = 0.91)

Gloss Side 41.7 (mean) (standard deviation = 5.6)

The differential in gloss values between the two surfaces of the sheet is best determined at larger angles (e.g. 85° as exemplified above), although this differential is also evident at other measurement angles (as for example 60°).

Under these conditions where one or more of the roller temperatures of the 3 roll stack (and especially the polishing roller) are kept at temperatures considerably below the glass transition temperature of the polymer, a very large difference in gloss was obtained between the two surfaces of the sheet. Increasing the roller temperatures toward the glass transition temperature of the thermoplastic polymer sheet leads to the eventual disappearance of such gloss differential on the two surfaces.

Example 2

The sheet of Example 1 was cut into sheets of size 5 feet by 14 feet (1 mm thick) and cold-laminated under pressure using a Seal laminator to rigid clear cast acrylic sheets (Plexiglass; Rohm and Haas) with thickness of one-eighth to one-half inch by adhering the high-gloss side to the clear acrylic sheet using an optically clear, cold-acting, pressure-sensitive laminating adhesive (Mactac PermaTrans IP-2100, Morgan Adhesives Co.) as the adhesive. A rigid composite sheet, without bubbles or fish-eyes, resulted having the matte surface on the outside. Such composite sheet was then used as a high-performance

front- and rear-projection screen exhibiting high brightness, contrast and visibility, even in high ambient light and direct light, which showed no "hot spots" and gave high visibility even at wide angles from the perpendicular to the screen. Removal of the matte surface from portions of the screen surface by buffing led to the production of dark image areas at the buffed regions, showing that the presence of the matte surface on the outside dramatically and usefully increases the brightness of images projected on the screen, and also showing the increased utility of screens made from the sheet of the present invention.

Example 3

Samples of the sheet of Example 1 varying in size from 1 ft by 1 ft to 3 ft by 3 ft were vacuum thermoformed using drape vacuum forming apparatus with a male mold placed below the glossy surface of the sheet. The horizontal sheet was heated on both sides to about 260°C to induce sag and the male mold then raised up and closed into the sheet to drape the sheet over it. A vacuum was pulled between the male mold and the sheet to ensure that the sheet attained a shape that faithfully followed the shape of the mold.

Shaped articles were easily made in this manner in the form of three-dimensional logos, faces etc. which retain the matte surface on the outside and the glossy surface on the inside without causing any deleterious reduction in the surface characteristics of the matte or the glossy surfaces.

As noted above, the present disclosure and examples are not intended to limit the scope of the invention, which is defined in the following claims and includes all lawful equivalents of the subject matter claimed.

Claims

1. Extruded thermoplastic or thermoset sheet having upper and lower surfaces exhibiting markedly different degrees of gloss such that one surface is high gloss while the other surface is matte, wherein the difference in gloss values between the surfaces, measured at an angle of 85°, is greater than about 40, and wherein said sheet is capable of passing light therethrough.
2. Sheet of claim 1 wherein said difference in gloss values is greater than about 50.
3. Sheet of claim 1 wherein said difference in gloss values is greater than about 60.
4. Sheet of claim 1 wherein said high gloss surface has a gloss value, measured at an angle of 85°, greater than about 70, and said matte surface has a gloss value, also measured at an angle of 85°, less than about 30.
5. Sheet of any of claims 1, 2, 3 or 4 in which the extruded sheet is a thermoplastic polymer composition comprising a thermoplastic matrix polymer throughout which are distributed particles having an average diameter of from 1 to 30 μm , the particles being blended with said matrix polymer in an amount of 0.1 to 50% by weight of the total composition.
6. Sheet of claim 5 wherein said particles are optically refractive.
7. Sheet of claim 5 wherein said particles comprise substantially spherical, optically refractive core-shell polymer particles that are distributed throughout said thermoplastic matrix polymer, said optically refractive particles having an average diameter of from 2 to 15 μm and a particle size distribution such that at least 90% by weight of the particles fall within $\pm 20\%$ of the average particle diameter, said optically refractive particles further having a core of rubbery alkyl acrylate polymer which is optionally crosslinked and/or grafted, and one or more shells, and said optically refractive particles being blended with said thermoplastic matrix polymer in an amount of 1 to 40% by weight of the total composition.

8. Sheet of claim 7 wherein said matrix polymer is substantially amorphous.
9. Sheet of claim 6 wherein said optically refractive particles are polymer particles comprising at least one polymeric phase having a refractive index (n_D^{25}) within ± 0.2 units of the refractive index of the matrix polymer but no closer than ± 0.003 units of the refractive index of the matrix polymer.
10. Sheet of claim 7 wherein the rubbery cores of said optically refractive particles comprise at least one polymeric phase having a refractive index (n_D^{25}) within ± 0.2 units of the refractive index of the matrix polymer but no closer than ± 0.003 units of the refractive index of the matrix polymer.
11. Sheet of claim 8 wherein the rubbery cores of said optically refractive particles comprise at least one polymeric phase having a refractive index (n_D^{25}) within ± 0.2 units of the refractive index of the matrix polymer but no closer than ± 0.003 units of the refractive index of the matrix polymer.
12. Sheet of claim 7 wherein the rubbery cores of said optically refractive particles comprise at least one polymeric phase having a refractive index (n_D^{25}) within ± 0.003 units of the refractive index of the matrix polymer.
13. Sheet of claim 8 wherein the rubbery cores of said optically refractive particles comprise at least one polymeric phase having a refractive index (n_D^{25}) within ± 0.003 units of the refractive index of the matrix polymer.
14. Sheet of claim 9 wherein the thermoplastic matrix polymer is an acrylic molding resin comprising a methyl methacrylate polymer, optionally further comprising a copolymerized alkyl acrylate.
15. Sheet of claim 10 wherein the thermoplastic matrix polymer is an acrylic molding resin comprising a methyl methacrylate polymer, optionally further comprising a copolymerized alkyl acrylate.
16. Sheet of claim 11 wherein the thermoplastic matrix polymer is an acrylic molding resin comprising a methyl methacrylate polymer, optionally further comprising a copolymerized alkyl acrylate.

17. Sheet of claim 12 wherein the thermoplastic matrix polymer is an acrylic molding resin comprising a methyl methacrylate polymer, optionally further comprising a copolymerized alkyl acrylate.

5 18. Composite sheet comprising an extruded sheet of claim 1 attached on said high gloss surface or said matte surface to a second sheet, said second sheet providing additional rigidity in said composite sheet and having a composition that is the same or different from said extruded sheet.

19. An optical viewing screen comprising the composite sheet of claim 18, said second sheet being attached to said high gloss surface of said extruded sheet and being
10 capable of passing light therethrough.

20. Composite sheet comprising an extruded sheet of claim 7 attached on said high gloss surface or said matte surface to a second sheet, said second sheet providing additional rigidity in said composite sheet and having a composition that is the same or different from said extruded sheet.

15 21. An optical viewing screen comprising the composite sheet of claim 20, said second sheet being attached to said high gloss surface of said extruded sheet and being capable of passing light therethrough.

22. Composite sheet comprising an extruded sheet of claim 10 attached on said high gloss surface or said matte surface to a second sheet, said second sheet providing
20 additional rigidity in said composite sheet and having a composition that is the same or different from said extruded sheet.

23. An optical viewing screen comprising the composite sheet of claim 22, said second sheet being attached to said high gloss surface of said extruded sheet and being capable of passing light therethrough.

25 24. A method of projecting an image onto an optical viewing screen comprising (a) providing an optical image light projector and (b) projecting an image from said light projector onto a viewing screen, said viewing screen comprising a sheet of claim 1.

25. The method of claim 24 wherein said image is projected onto the high gloss surface of said screen.

26. The method of claim 24 wherein said image is projected onto the matte surface of said screen.

5 27. The method of claim 24 wherein said viewing screen is substantially flat.

28. The method of claim 24 wherein said viewing screen comprises at least one non-flat shaped portion onto which said image is projected.

29. A method of projecting an image onto an optical viewing screen comprising (a) providing an optical image light projector and (b) projecting an image from
10 said light projector onto a viewing screen, said viewing screen comprising a sheet of claim 5.

30. The method of claim 29 wherein said image is projected onto the high gloss surface of said screen.

31. The method of claim 29 wherein said image is projected onto the matte
15 surface of said screen.

32. The method of claim 29 wherein said viewing screen is substantially flat.

33. The method of claim 29 wherein said viewing screen comprises at least one non-flat shaped portion onto which said image is projected.

34. In a rear projection viewing system comprising an optical image light
20 projector and a viewing screen, wherein said light projector projects an image onto a rear surface of said screen opposite the normal front viewing surface of said screen, the improvement comprising providing, as said viewing screen, a screen comprising a sheet of claim 1.

35. The system of claim 34, wherein said projection viewing system is a rear
25 projection television set.

36. The system of claim 34, wherein said image is projected onto the high gloss side of said sheet.

37. In a front projection viewing system comprising an optical image light projector and a viewing screen, wherein said light projector projects an image onto a front surface of said screen that is a normal viewing surface of said screen, the improvement comprising providing, as said viewing screen, a screen comprising a sheet of claim 1.

38. The system of claim 37, wherein said image is projected onto the matte side of said sheet.